68–3

THE EFFECT OF PRESSURE ON THE ELECTRICAL RESISTANCE OF SINGLE METAL CRYSTALS AT LOW TEMPERATURE.

BY P. W. BRIDGMAN.

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CONTENTS.

INTRODUCTION.

In this paper measurements are presented of the effect of hydrostatic pressure up to 7000 kg/cm^2 at $-78°$ and $-183°$ (solid CO_2 and liquid O_2 temperatures) on the electrical resistance of the noncubic metals Zn, Cd, Sn, Bi, Sb, As, and Te in the single crystal form. Except for As, two orientations were examined for each metal, so that the effect of pressure on resistance for all directions of current flow in the crystal is thereby determined. These measurements constitute an extension of measurements previously made in the same range of pressure and temperature for a number of metals crystallizing in the cubic system.[1] The apparatus and general method were the same as formerly and therefore need not be described again.

The preparation of the single crystals requires a short discussion since the small size demanded a modification of the method formerly used. The length must not be greater than 2.5 cm., and the diameter must be proportionally small to give a resistance high enough for the requisite accuracy. The diameter of most of the crystal rods was of the order of 1 mm. They were cast in pyrex tubing of this diameter by the same method as that by which my other crystals have been made,[2] namely by slow lowering out of a furnace. The pyrex tubing was bent at a number of places so as to form a broken line, each segment being about 2.5 cm. long, with the orientations of

the segments spaced more or less uniformly over the entire possible range.   In this way a single casting gives crystal rods of many orientations.   The formation of single crystal castings of this small diameter is much easier than the formation of larger diameters, since the chance of occurrence of new nuclei is much less with the small diameter, so that the probability of a switch from one orientation to another is much decreased.   In fact, all the castings attempted were single grains without any switches.   There are, however, compensating difficulties in the use of such small crystals.   If the metal has a well developed cleavage, as do Zn, Bi, Sb, As, and Te, the orientation of the rod may be determined at once by locating the cleavage plane. But Cd and Sn have no cleavage.   The former method was to determine the reflection pattern of each rod, but this method is hardly practical now because of the difficulty of locating on such small rods enough regular reflections to permit a certain identification of the axis.   A simple modification of the reflection method was found feasible.   The reflection pattern of the entire casting, as it comes from the furnace, was determined by the method previously applied to single rods.   This was always easy, because out of the dozen or more directions there were sure to be some favorably situated with regard to any particular reflection direction, so that the entire reflection pattern could be located, and the axis certainly determined. This axis was then marked, and the casting broken into the separate straight rods, noting the orientation of each rod as it was broken off. This method does not permit as clean a location of each separate direction in the reflection pattern as was formerly possible with the individual bare rods, because of the confusion incident to reflection through the glass tubing, but this is compensated by the possibility of locating all the faces, so that the finally determined orientation should be as accurate as before, within a degree or less.

Another detail of technique that had to be modified because of the small size of the crystal is the method of removing from the glass mold.   The glass cannot be cracked away, as was formerly done, without danger of producing a serious amount of bending or other distortion of the rod.   The glass was therefore ground off; this was conveniently done by rubbing the glass tube with the crystal in it on a plate glass with carborundum powder until the metal was just reached, and then rubbing through again from the opposite side, when the glass tube drops off.   The naked crystal rod, which is exceedingly deformable, was then slipt at once into a protecting trough, made by grinding off one side of a glass tube of internal diameter

slightly greater than the diameter of the crystal. The current leads were then attached by soldering at the ends, and the potential leads by soldering at the sides through the open side of the trough.

Because of the low resistance of the specimens, which is much enhanced at the low temperatures, much larger measuring currents were necessary than formerly; these reached at the maximum about 0.4 amp. This large current did not, however, introduce undesirable parasitics, and the accuracy was in fact in many cases better than before.

The methods of computation, by which the effect of pressure on the measured resistance in two different arbitrary directions is to be reduced to the effect of pressure on the specific resistance parallel and perpendicular to the crystal axis, are somewhat complicated, and involve several steps. The effect of pressure on the *measured* resistance (that is, the resistance of a rod with terminals attached to the rod) of a crystal rod of given orientation must first be converted into the effect of pressure on the specific resistance in the same direction. This involves two corrections; one for the effect of pressure on the linear dimensions of the rod, and the other for the effect of pressure on the orientation of the rod, for obviously the angle between the length of the rod and the crystal axis changes with pressure. The method of computing both these corrections has been previously given.[3] The fractional increase of resistance under unit increment of pressure arising from change of dimensions is:

$$2 (S_{11} + S_{12}) \cos^2 \theta + 2S_{13} \sin^2 \theta + S_{33} (1 - 2 \cos^2 \theta),$$

and the corresponding fractional increase arising from the change of angle produced by pressure is:

$$2 \frac{\rho_{90°} - \rho_{0°}}{\rho} \sin^2 \theta \cos^2 \theta [S_{33} + S_{13} - S_{11} - S_{12}].$$

Here the S's are the elastic constants in Voigt's notation, θ is the angle between the crystal axis and the length of the rod, and ρ is specific resistance. The elastic constants have been previously determined at room temperature and for low stresses, and are tabulated in the paper just referred to. The correction for the change of angle is usually much smaller than that for the change of dimensions, and is in many cases negligible. The maximum correction is for Cd, where both corrections together amount to 37%. Strictly, the elastic constants are functions of pressure and temperature, but the variation is probably not large, and since it has not been determined experi-

mentally, the best that could be done was to assume that the correction is linear with pressure and the same at all temperatures.

The effect of pressure on *specific resistance* having thus been determined for the two given orientations, it remains to find the effect of pressure on the specific resistance in the parallel and perpendicular directions, these being the two independent parameters of greatest simplicity. This may be done by means of the general relations connecting resistance and orientation

$$\rho_{\theta 1} = \rho_{0^\circ} \cos^2 \theta_1 + \rho_{90^\circ} \sin^2 \theta_1$$

$$\rho_{\theta 2} = \rho_{0^\circ} \cos^2 \theta_2 + \rho_{90^\circ} \sin^2 \theta_2,$$

which give

$$\rho_{0^\circ} = \frac{\rho_{\theta 1} \sin^2 \theta_2 - \rho_{\theta 2} \sin^2 \theta_1}{\cos^2 \theta_1 \sin^2 \theta_2 - \cos^2 \theta_2 \sin^2 \theta_1}$$

$$\rho_{90^\circ} = \frac{\rho_{\theta 1} \cos^2 \theta_2 - \rho_{\theta 2} \cos^2 \theta_1}{\cos^2 \theta_2 \sin^2 \theta_1 - \cos^2 \theta_1 \sin^2 \theta_2}.$$

These equations connecting ρ_{0° and ρ_{90° with $\rho_{\theta 1}$ and $\rho_{\theta 2}$ hold at every pressure. But $\rho_{\theta 1}$ and $\rho_{\theta 2}$ are now known as functions of pressure because of the corrections for distortion which have just been discussed, so that ρ_{0° and ρ_{90° may at once be found also as functions of pressure. In particular, if $\rho_{\theta 1}$ and $\rho_{\theta 2}$ are linear or second degree functions of the pressure then ρ_{0° and ρ_{90° are also.

It is to be noticed that the calculation demands the absolute values of $\rho_{\theta 1}$ and $\rho_{\theta 2}$ as well as the pressure coefficients. The relative resistance of the different orientations at atmospheric pressure was measured as a function of temperature, as well as the pressure effect, and this, combined with the previously measured resistance[4] at atmospheric pressure at temperatures above 0° C gives the required absolute values at lower temperatures.

Because of the necessary approximations in reducing from measured to specific resistance parallel and perpendicular, I have thought it best to record in the following both the actual results for the effect of pressure on the measured resistance as well as the values computed therefrom for specific resistance parallel and perpendicular. The measured resistances stand; if in the future the dependence of elastic constants on temperature and pressure should be determined, the specific resistances as given in the following may be recomputed and improved.

The routine of the pressure measurements was the same as in the preceding paper. One general difference between the previous measurements with cubic metals, which were usually in the form of drawn wires, and the present measurements needs special comment, namely the fact that seasoning effects on the very first application of pressure were much less for the crystals than for the wires. This is in accord with general experience that a single crystal, if it has been properly handled, is in a state of complete ease, and needs no seasoning. The tendency for the zero point to lie off the curve drawn through the pressure points was also much less marked for the single crystals than for the wires, and there was no consistency in the direction of deviation.

DETAILED DATA.

Zinc. The single crystals were made from spectroscopically pure Zn obtained from the New Jersey Zinc Co. This was obtained through the courtesy of Mr. Cyr, and I take this opportunity of expressing my indebtedness to him. The purity is doubtless materially higher than that of the Zn used in the previous work, although there was no reason to suspect an amount of impurity in the "Kahlbaum" zinc previously used sufficient to produce appreciable error. Before casting, the metal was filtered in the molten condition, and thoroughly outgassed in a diffusion pump vacuum. This preliminary outgassing plays an important part in permitting the formation of geometrically perfect crystals without blow holes. The same procedure was followed with all the other metals.

Runs were made on two samples, the axis being perpendicular and at 18° to the length. Various accidents, which culminated in the rupture of the connecting pipe, made readings on the perpendicular sample, particularly at CO_2 temperature, less complete than usual. However the entire pressure range was covered and it did not appear that the uncertainty in the results was great enough to demand another set-up. The run at CO_2 temperature on the perpendicular sample was not good enough to justify more than drawing the best straight line through the experimental points, but the other three runs, one on the perpendicular and two on the 18° orientation, gave curves distinctly not linear, but of the second degree in the pressure. The average deviation of the points of these three runs from second degree curves was a small fraction of one per cent.

The numerical results are now given in Table I.

TABLE I.
Zinc.

Angle between axis and length	Temp. °C	Relative Effect of Pressure on Measured Resistance	Average Coefficient of Measured Resistance 0–7000 kg/cm²	Relative Effect of Pressure on Specific Resistance	Specific Resistance at 0 Pressure	Relative Specific Resistance at 0 Pressure
90°	0°				5.386×10^{-6}	1.0000
	$-78°.44$	$-5.38 \times 10^{-6}p$	-5.38×10^{-6}	$-6.67 \times 10^{-6}p$	3.657	.6788
	$-182°.98$	$-7.53 \times 10^{-6}p + 6.9 \times 10^{-11}p^2$	-7.04	$-8.82 \times 10^{-6}p + 6.9 \times 10^{-11}p^2$	1.322	.2455
18°	0°				5.568	1.0000
	$-78°.54$	$-11.06 \times 10^{-6}p + 13.1 \times 10^{-11}p^2$	-10.14	$-10.34 \times 10^{-6}p + 13.1 \times 10^{-11}p^2$	3.784	.6797
	$-182°.95$	$-12.76 \times 10^{-6}p + 17.5 \times 10^{-11}p^2$	-11.53	$-12.04 \times 10^{-6}p + 17.5 \times 10^{-11}p^2$	1.665	.2922
90°	0°			As above	5.386	1.0000
	$-78°.30$				3.660	.6794
	$-182°.80$				1.325	.2459
0°	0°				5.589	1.0000
	$-78°.30$			$-10.72 \times 10^{-6}p + 14.4 \times 10^{-11}p^2$	3.804	.6807
	$-182°.80$			$-12.31 \times 10^{-6}p + 18.4 \times 10^{-11}p^2$	1.703	.3047

Cadmium. The material was from Kahlbaum, grade "Kahlbaum." The procedure in casting the single crystals was canonical in every way, except that the furnace was filled with CO_2 during the melting and filling of the mold in order to avoid oxidation.

Previous measurements on cadmium at temperatures above 0° C had disclosed an unusual situation in that there are two polymorphic transitions,[5] the lower one taking place at about 3000 kg/cm^2. It is a peculiarity of these transitions that when the original modification is restored by a release of pressure the original crystal orientation is completely lost, the originally single crystal becoming a haphazard aggregate. It follows that no pressure measurements of significance can be made on the normal low pressure modification unless the pressure is continually kept below 3000 kg/cm^2, a consideration that was not properly appreciated soon enough in making the former measurements.

On the first applications of pressure at CO_2 temperature unusual care was therefore taken. The pressure steps were made unusually short and 12 readings were made in the first 3000 kg. instead of the usual 4. No discontinuities were found, however, and beyond 3000 the pressure steps were made longer, still with no trace of discontinuity. The same was found with both crystals at both temperatures: no evidence whatever of a transition was found. The obvious explanation is that the transition is suppressed at low temperatures by internal viscosity.

Runs on both orientations at both temperatures were accomplished without accident of any kind. The average deviation from smooth curves of all 71 points of the 4 runs, including the zero point deviations which were by far the largest, was 0.3% of the maximum pressure effect. Within experimental error the measurements can be reproduced by second degree curves, except for the 25° orientation at CO_2 temperature. Here the curvature at the low pressure end of the range is somewhat less and at the high pressure end somewhat greater than indicated by the second degree formula, but the deviation is so small that no attempt was made to reproduce it by the introduction of higher terms. The second degree formula given in the table is that corresponding to a curve drawn through the two end and the mid points.

The numerical results are collected in Table II.

Tin. The material was "Kahlbaum" stock, treated and crystallized in the usual way. The axis of the first specimen was inclined at 82° to the length. There were zero point irregularities of the order of 5% of the maximum effect. The average numerical deviation of

TABLE II.

CADMIUM.

Angle between axis and length	Temp. °C	Relative Effect of Pressure on Measured Resistance	Average Coefficient of Measured Resistance 0–7000 kg/cm²	Relative Effect of Pressure on Specific Resistance	Specific Resistance at 0 Pressure	Relative Specific Resistance at 0 Pressure
89°	0°				6.289×10^{-6}	1.0000
	-78.35	$-7.67 \times 10^{-6}p + 6.1 \times 10^{-11}p^2$	-7.24×10^{-6}	$-10.38 \times 10^{-6}p + 6.1 \times 10^{-11}p^2$	4.339	.6900
	$-182°.68$	$-9.01 \times 10^{-6}p + 11.8 \times 10^{-11}p^2$	-8.19	$-11.72 \times 10^{-6}p + 11.8 \times 10^{-11}p^2$	1.793	.2850
25°	0°				7.359	1.0000
	$-78°.28$	$-12.90 \times 10^{-6}p + 20.8 \times 10^{-11}p^2$	-11.44	$-13.21 \times 10^{-6}p + 20.8 \times 10^{-11}p^2$	5.078	.6902
	$-182°.83$	$-13.13 \times 10^{-6}p + 15.9 \times 10^{-11}p^2$	-12.01	$-13.44 \times 10^{-6}p + 15.9 \times 10^{-11}p^2$	2.123	.2886
90°	0°				6.289	1.0000
	$-78°.30$			$-10.37 \times 10^{-6}p + 6.1 \times 10^{-11}p^2$	4.340	.6899
	$-182°.80$			$-11.71 \times 10^{-6}p + 11.8 \times 10^{-11}p^2$	1.791	.2850
0°	0°				7.593	1.0000
	$-78°.30$			$-13.72 \times 10^{-6}p + 23.4 \times 10^{-11}p^2$	5.240	.6903
	$-182°.80$			$-13.75 \times 10^{-6}p + 16.6 \times 10^{-11}p^2$	2.195	.2891

the other points from smooth curves was 0.3% of the maximum effect. At liquid O_2 temperature the relation between pressure and resistance was of the second degree within the limits of error. At CO_2 temperature there was perceptibly too much curvature at the higher pressures, as had also been found with cadmium, but the effect was so small that no attempt was made to get it into a formula. The other sample, with the axis at 17° to the length, showed on the first application of pressure at CO_2 temperature consistent seasoning effects much larger than normal, the initial zero lying below the final zero by about 10% of the maximum effect. The points with decreasing pressure were alone retained; these lay on a straight line with an average deviation of 0.7% of the maximum effect. At liquid O_2 temperature the seasoning effects entirely disappeared, and there was no zero disturbance, the average deviation of all points from a second degree curve being 0.3% of the maximum effect.

The numerical results are given in Table III.

Bismuth. This material had been prepared by a double electrolytic deposition; the original source of the material was a mixture of bismuth "Kahlbaum" and electrolytic bismuth from the U. S. Metals Refining Co. The regular casting procedure was followed. Runs were made on three samples. Three runs, at liquid O_2, CO_2, and liquid O_2 temperatures again, were made on the first sample, the axis of which was at 65° to the length. Both runs at liquid O_2 temperature showed considerable difference between the points obtained with increasing and decreasing pressure, the points of either set separately lying on a smooth curve. The maximum difference between ascending and descending branches was about 8% of the maximum effect. At CO_2 temperature the same phenomenon was exhibited, but in much less degree. This is unusual, for the irregularity is usually greatest at the higher temperature. It is also most unusual for the irregularity not to disappear on the second application of pressure at liquid O_2 temperature. No explanation was found of this anomalous behavior, so that it seemed best to discard the results for this crystal altogether. The results, however, were not inconsistent within their own irregularity with the results for the other two samples. The other two orientations were at 78° and 14.5° to the axis. The readings with these were very much more regular than for the first sample. There was, however, still more irregularity of the zero than with any of the other metals of this series. The maximum zero irregularity was shown by the 14.5° orientation at liquid O_2 temperature, where the maximum discrepancy of six

TABLE III.

Tₙ.

Angle between axis and length	Temp. °C	Relative Effect of Pressure on Measured Resistance	Average Coefficient of Measured Resistance 0–7000 kg/cm²	Relative Effect of Pressure on Specific Resistance	Specific Resistance at 0 Pressure	Relative Specific Resistance at 0 Pressure
82°	0°				13.01×10^{-6}	1.0000
	$-78°.30$	$-9.36 \times 10^{-6} p + 10.2 \times 10^{-11} p^2$	-8.64×10^{-6}	$-10.02 \times 10^{-6} p + 10.2 \times 10^{-11} p^2$	8.684	.6674
	$-182°.90$	$-10.19 \times 10^{-6} p + 16.7 \times 10^{-11} p^2$	-9.01	$-10.85 \times 10^{-6} p + 16.7 \times 10^{-11} p^2$	3.239	.2490
17°	0°				9.430	1.0000
	$-78°.38$	$-9.79 \times 10^{-6} p$	-9.79	$-10.33 \times 10^{-6} p$	6.367	.6752
	$-182°.73$	$-11.06 \times 10^{-6} p + 12.2 \times 10^{-11} p^2$	-10.20	$-11.60 \times 10^{-6} p + 12.2 \times 10^{-11} p^2$	2.478	.2628
90°	0°				13.08	1.0000
	$-78°.30$			$-10.16 \times 10^{-6} p + 10.4 \times 10^{-11} p^2$	8.736	.6678
	$-182°.80$			$-10.84 \times 10^{-6} p + 16.8 \times 10^{-11} p^2$	3.255	.2489
0°	0°				9.088	1.0000
	$-78°.30$			$-10.38 \times 10^{-6} p + 13.8 \times 10^{-11} p^2$	6.147	.6764
	$-182°.80$			$-11.66 \times 10^{-6} p + 11.9 \times 10^{-11} p^2$	2.404	.2646

readings at 100 kg. or less was 4% of the total resistance.   At higher
pressures the regularity was much better.   The 78° sample showed in
general much the same sort of behavior as the discarded 65° sample,
there being a difference between the ascending and descending points,
both of which by themselves lay on smooth curves.   The maximum
difference between ascending and descending points at CO_2 tempera-
ture was 2.7% of the maximum effect, and at liquid O_2 temperature
4.2%.   Since it has been my general experience that the descending
points are much more likely to be correct, the ascending points were
discarded in the final computation.   The 14.5° orientation had no
such consistent difference between ascending and descending points,
the irregularities being distributed more at random between the two
sets.   The average numerical departure from a smooth curve was
0.7% at both temperatures.   The corresponding departure of the
points that were retained of the 78° orientation was so small as to
be inappreciable on the scale of graphical construction employed.
At liquid O_2 temperature the points of the 78° specimen lay sensibly
on a second degree curve, and similarly the points of the 14.5° speci-
men at CO_2 temperature.   The other two runs deviated very notice-
ably from the second degree, and in each case the deviation was in
the same direction, in that the curvature is greater at the lower pres-
sure and less at the higher pressure than would be demanded by a
second degree relation.   No attempt was made to find a formula
for the non-second degree results, but in the following they are tabu-
lated at 1000 kg. intervals.

The numerical results are given in Table IV.

Antimony.   The material was the "Kahlbaum" grade.   Except
for the fact that the casting was made in quartz instead of pyrex, the
procedure was the same as with the other metals.   The extreme ease
of cleavage makes the orientations with cleavage across the rod very
difficult to handle, particularly in these small diameters, and the
highest orientation that was measured was 41° (49° between cleavage
plane and length).   The other orientation was 87°.   All four runs
departed very markedly from the second degree relation and always
in the same direction, the curvature being greater at the low pressure
end of the curves; this is in the same direction as the departures
shown by bismuth.   The same irregularity with increasing pressure
exhibited by bismuth was shown by this also, although not to so
marked a degree.   There was also some scattering of the zero, al-
though again not nearly as much as by bismuth.   The maximum
deviation between ascending and descending points of the 41° speci-

TABLE IV.

Bismuth.

Angle between axis and length	Temp. °C	Relative Effect of Pressure on Measured Resistance		Average Coefficient of Measured Resistance 0–7000 kg/cm²	Relative Effect of Pressure on Specific Resistance		Specific Resistance at 0 Pressure	Relative Specific Resistance at 0 Pressure
		p	Resis		p	Resis		
78°	0°	0	1.0000		0	1.0000	101.3×10^{-6}	1.0000
		1000	1.0115		1000	1.0100		
		2000	1.0257		2000	1.0228		
		3000	1.0426		3000	1.0382		
		4000	1.0619		4000	1.0561		
		5000	1.0825		5000	1.0752		
		6000	1.1040		6000	1.0953		
		7000	1.1268		7000	1.1166		
	-78.30			$+18.11\times10^{-6}$			70.87	.6998
	-182.75	$+15.31\times10^{-6}p+239\times10^{-11}p^2$		$+32.06$	$+13.86\times10^{-6}p+239\times10^{-11}p^2$		36.98	.3583
14°.5	0°	$+17.14\times10^{-6}p+167\times10^{-11}p^2$			$+17.32\times10^{-6}p+167\times10^{-11}p^2$		125.1	1.0000
	-78.30			$+28.86$			86.06	.6877
	-192.85	p	Resis		p	Resis		
		0	1.0000		0	1.0000		
		1000	1.0235		1000	1.0237		
		2000	1.0528		2000	1.0532		
		3000	1.0874		3000	1.0879	$+39.03$	41.44	.3312
		4000	1.1269		4000	1.1276		
		5000	1.1712		5000	1.1721		
		6000	1.2200		6000	1.2211		
		7000	1.2732		7000	1.2745		

TABLE IV.—BISMUTH.—*Continued.*

Angle between axis and length	Temp. °C	Relative Effect of Pressure on Measured Resistance	Average Coefficient of Measured Resistance 0–7000 kg/cm²	Relative Effect of Pressure on Specific Resistance		Specific Resistance at 0 Pressure	Relative Specific Resistance at 0 Pressure
				p	*Resis*		
90°	0°	—	—	—	—	100.1	1.0000
	− 78°.30	—		0	1.0000		—
				1000	1.0095		
				2000	1.0216	70.08	.7001
				3000	1.0365		
				4000	1.0537		
				5000	1.0721		
				6000	1.0916		
				7000	1.1114		
	− 182°.80	—		0	1.0000		—
				1000	1.0159		
				2000	1.0365		
				3000	1.0618	36.02	.3598
				4000	1.0820		
				5000	1.1268		
				6000	1.1664		
				7000	1.2111		

TABLE IV.—Bismuth.—*Continued.*

Angle between axis and length	Temp. ° C	Relative Effect of Pressure on Measured Resistance	Average Coefficient of Measured Resistance 0–7000 kg/cm²	Relative Effect of Pressure on Specific Resistance		Specific Resistance at 0 Pressure	Relative Specific Resistance at 0 Pressure
				p	*Resis*		
0°	0°	—	—	0	1.0000	126.8	1.0000
				1000	1.0195		
				2000	1.0424		
				3000	1.0687		
				4000	1.0982		
				5000	1.1316		
				6000	1.1586		
				7000	1.2084		
	− 78°.30	—	—	—	—	87.14	.6873
	− 182°.80	—	—	0	1.0000	41.78	.3295
				1000	1.0241		
				2000	1.0542		
				3000	1.0895		
				4000	1.1297		
				5000	1.1750		
				6000	1.2244		
				7000	1.2783		

men was 1.2% of the maximum at CO_2 temperature, and the maximum deviation by the 87° specimen 7% at liquid O_2 temperature. The descending points only were used, as in the case of bismuth, and again the average deviation from a smooth curve was inappreciable on the graphical scale employed, and was not more than a fraction of a tenth of a per cent.

The results are given in Table V.

Arsenic. It has not yet been found possible to prepare single crystals of dimensions suitable for the low temperature apparatus in which the cleavage plane runs across the rod at any considerable angle. These measurements refer to only a single orientation with the cleavage plane parallel to the length. In a previous paper[6] measurements have been given at 0° and 95° C for the resistance of single crystal arsenic up to 12000 kg/cm². The specimen used here was the same as one of the pieces previously measured. Arsenic is highly anomalous; both compressibility and electrical resistance in the direction of the cleavage plane (that is, the direction measured here) showing breaks, the interval from 0 to 12000 kg/cm² consisting of ranges in each of which the dimensions or resistance vary linearly with pressure, with different slopes in the different ranges. These anomalous effects rapidly disappear as the orientation swings toward the perpendicular.

Exactly the same phenomenon was found at CO_2 and liquid O_2 temperatures. One break in the slope of the curve giving resistance as a function of pressure occurs at each temperature in the pressure range up to 7000. Previously two breaks had been found up to 12000, which means three linear ranges. The middle range was shorter and somewhat more in doubt as compared with the two extreme ranges. It is not possible to say whether the two ranges found now at the lower temperatures correspond to the two low pressure ranges of the higher temperatures or whether the former middle range has been so displaced by temperature as to be absorbed by the low and the high pressure ranges. The latter seems to me somewhat the more probable.

At CO_2 temperature there were considerable seasoning effects at the low pressures, as is usual, so that the points obtained with increasing pressure did not show a very distinct break. The points with decreasing pressure, however, lay without question on two rather well marked different lines. At liquid O_2 temperature the seasoning effects were less, and the location of the break between the two separate ranges could be established with more certainty.

TABLE V.
ANTIMONY.

Angle between axis and length	Temp. °C	Relative Effect of Pressure on Measured Resistance		Average Coefficient of Measured Resistance 0–7000 kg/cm²	Relative Effect of Pressure on Specific Resistance		Specific Resistance at 0 Pressure	Relative Specific Resistance at 0 Pressure
		p	Resis		p	Resis		
87°	0°						38.63×10^{-6}	1.0000
	$-78°.26$	0	1.0000		0	1.0000		
		1000	1.0055		1000	1.0039		
		2000	1.0154		2000	1.0122		
		3000	1.0290	$+15.10 \times 10^{-6}$	3000	1.0240	24.67	.6390
		4000	1.0457		4000	1.0391		
		5000	1.0651		5000	1.0569		
		6000	1.0852		6000	1.0753		
		7000	1.1057		7000	1.0942		
	$-182°.76$	0	1.0000		0	1.0000		
		1000	1.0032		1000	1.0016		
		2000	1.0148		2000	1.0115		
		3000	1.0393	$+33.49$	3000	1.0344	8.70	.2251
		4000	1.0770		4000	1.0704		
		5000	1.1240		5000	1.1158		
		6000	1.1763		6000	1.1664		
		7000	1.2344		7000	1.2229		

TABLE V.—ANTIMONY.—Continued.

Angle between axis and length	Temp. °C	Relative Effect of Pressure on Measured Resistance		Average Coefficient of Measured Resistance 0–7000 kg/cm²	Relative Effect of Pressure on Specific Resistance		Specific Resistance at 0 Pressure	Relative Specific Resistance at 0 Pressure
		p	Resis		p	Resis		
41°	0°	—	—	—	—	—	33.28	1.0000
							—	—
	− 78°.32	0	1.0000		0	1.0000		
		1000	1.0115		1000	1.0133		
		2000	1.0272	+22.61	2000	1.0309	21.20	.6374
		3000	1.0475		3000	1.0530		
		4000	1.0716		4000	1.0790		
		5000	1.0985		5000	1.1077		
		6000	1.1277		6000	1.1387		
		7000	1.1593		7000	1.1722		
							—	—
	− 182°.70	0	1.0000		0	1.0000		
		1000	1.0057		1000	1.0075		
		2000	1.0210		2000	1.0247		
		3000	1.0490	+37.66	3000	1.0544	7.525	.2262
		4000	1.0917		4000	1.0991		
		5000	1.1430		5000	1.1522		
		6000	1.2010		6000	1.2120		
		7000	1.2636		7000	1.2765		
90°	0°	—					38.66	1.0000
							—	—
	− 78°.30				0	1.0000		
					1000	1.0039		
					2000	1.0121		
					3000	1.0239	24.69	.6390
					4000	1.0390		
					5000	1.0567		
					6000	1.0750		
					7000	1.0940		

TABLE V.—ANTIMONY.—Continued.

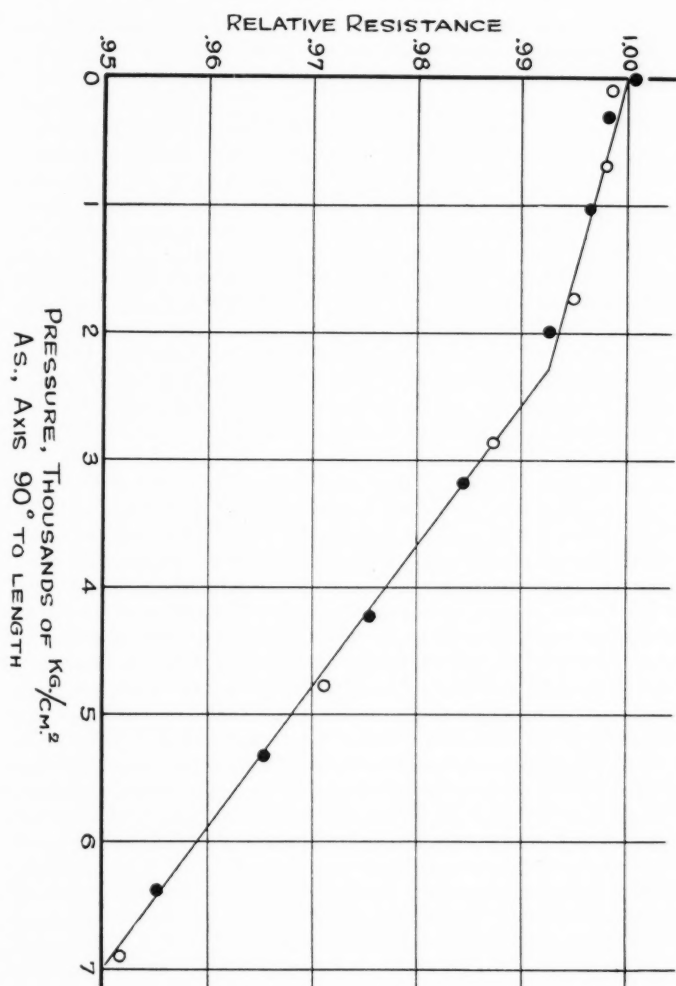| Angle between axis and length	Temp. °C	Relative Effect of Pressure on Measured Resistance	Average Coefficient of Measured Resistance 0–7000 kg/cm²	Relative Effect of Pressure on Specific Resistance		Specific Resistance at 0 Pressure	Relative Specific Resistance at 0 Pressure
				p	Resis		
90°	−182°.80			0	1.0000	8.706	.2251
				1000	1.0016		
				2000	1.0114		
				3000	1.0343		
				4000	1.0703		
				5000	1.1157		
				6000	1.1662		
				7000	1.2227		
0°	0°					29.23	1.0000
	−78°.30			0	1.0000	18.55	.6362
				1000	1.0228		
				2000	1.0498		
				3000	1.0823		
				4000	1.1193		
				5000	1.1590		
				6000	1.2027		
				7000	1.2510		
	−182°.80			0	1.0000	6.631	.2269
				1000	1.0134		
				2000	1.0378		
				3000	1.0743		
				4000	1.1275		
				5000	1.1884		
				6000	1.2573		
				7000	1.3298		

FIGURE 1.   Relative resistance at − 82.8° of single crystal arsenic, hexagonal axis perpendicular to the length.

The experimental points at liquid O_2 temperature are shown in Figure 1. The ranges and the coefficients are as follows:

As, axis perpendicular to length.

$$- \quad 78.3°, 0 - 3540, \Delta R/R \ (0, - \quad 78°.3) = - 1.92 \times 10^{-6}p.$$

$$3540 - 7000, \Delta R/R \ (0, - \quad 78°.3) = - 3.24 \times 10^{-6}p.$$

$$- 182.8° \ \ 0 - 2360, \Delta R/R \ (0, - 182°.8) = - 3.34 \times 10^{-6}p.$$

$$2360 - 7000, \Delta R/R \ (0, - 182°.8) = - 8.86 \times 10^{-6}p.$$

The relative resistances at atmospheric pressure at these temperatures were respectively .6501 and .2114 in terms of the resistance at 0° C at atmospheric pressure as unity.

The pressure at which the first break occurs is a more or less well defined function of pressure. The numerical values are as follows:

Pressure	Temperature
7100 kg/cm²	75° C
5500	0
3540	− 78.3
2360	− 182.8

If these points are plotted, a fair straight line will be obtained passing through 0° Abs.

Tellurium. The crystals were made from "Kahlbaum" material. They were cast in pyrex tubes of about 1.2 mm. diameter like the other metals. One casting proved sufficient, so that the two pieces measured below are different orientations from the identical crystal. The furnace was filled with a protecting atmosphere of CO_2 during the filling of the tube, and the rate of lowering was about 10 cm. per hour. The cleavage system of tellurium differs from that of the other metals of this paper in that there are three planes of easy cleavage, instead of one, each of the three planes being parallel to the trigonal axis, so that the intersections of the three planes form triangular prisms with edges parallel to the axis. Unless the axis is very nearly parallel to the length, one of the three cleavage planes will cut across the rod at a fairly high angle, which means, in rods of this small diameter, very easy fracture. The usual method of grinding away the glass tubes proved to be too severe, resulting in frequent breaking. The method finally adopted was to dissolve away the glass in hydrofluoric acid, the tellurium fortunately proving not to be attacked. The crystals obtained in this way were highly satisfactory in appear-

ance, with clean mirror-like cleavage planes, and were much better than I have ever obtained before. The improvement is probably to be ascribed partly to higher purity in the material, and partly to the smaller diameter.

Some difficulty was encountered in attaching the leads. Tellurium cannot be soldered, but it is known to stick directly to copper or platinum, when these are heated hot enough to melt their way into the tellurium. Platinum leads were attached by fusing in this way, but although they proved satisfactory on the initial application of pressure, high resistance developed on subsequent applications, doubtless an effect of cracking due to differential compressibility between tellurium and platinum. Experiment showed that silver very readily alloys with tellurium, in fact, the alloying action is so rapid that fine silver wires cannot be fused into the tellurium, but melt back and drop off. Finally fine platinum wire (0.005 cm. in diameter) was first coated with silver by fusing the silver, and then melted into the tellurium with a diminutive loop of nichrome heated to incandescence. This was entirely satisfactory; apparently the thin layer of alloy on the surface of the platinum is so tenacious as not to be entirely cracked by the differential compressibility.

The specific resistance of tellurium is so high that a modification of the regular potentiometer method of measurement was necessary. The simplest modification imaginable proved satisfactory. The potential drop across the tellurium under a known current was equalized to the potential drop produced by the same current across a variable resistance. An easy modification of the regular potentiometer connections proved feasible, which it is not necessary to describe in further detail.

The effect of pressure on the resistance of single crystal tellurium has not been measured previously because suitable specimens had not been available. The usual measurements at $-78.3°$ and $-182.8°$ were therefore supplemented by a run at $0°$ C in the low pressure apparatus, pressure transmitted with nitrogen, to a maximum of 7000 kg/cm^2. The results obtained were so interesting, showing very large changes of resistance with both temperature and pressure, that it appeared desirable to extend the pressure and temperature range. The specimens were therefore set up in the regular high pressure apparatus, and the run at $0°$ repeated to 12000, petroleum ether transmitting the pressure, and a similar run was made at $95°$.

The effects are so large that the logarithm of the resistance may be conveniently shown as a function of pressure rather than the re-
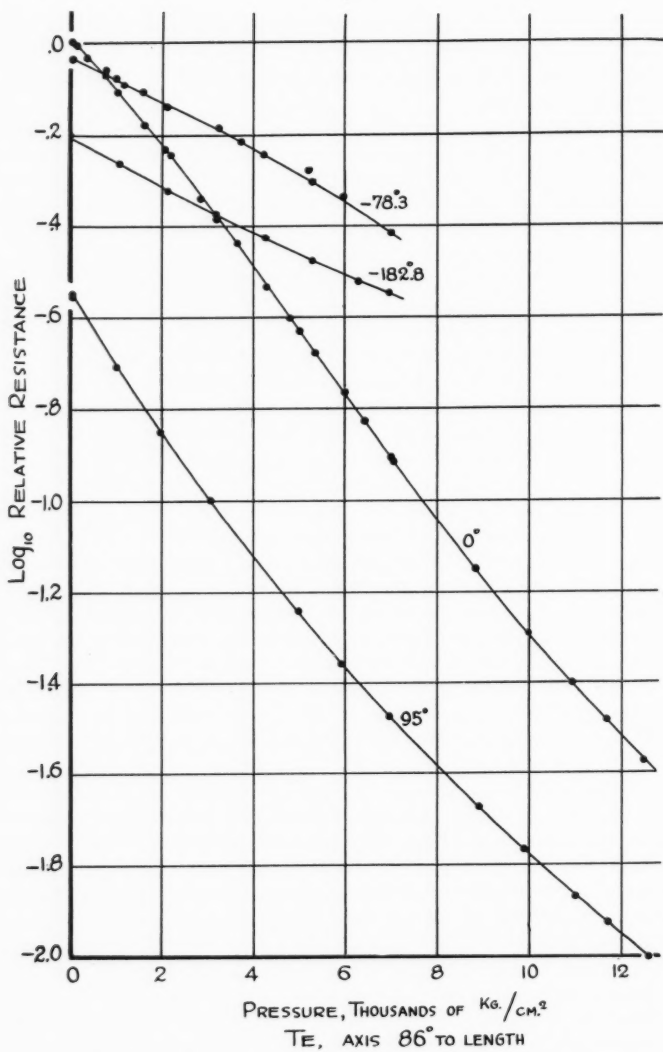
FIGURE 2.   Logarith to the base 10 of the relative resistance of single crystal tellurium, axis 86° to the length, as a function of pressure at several temperatures.
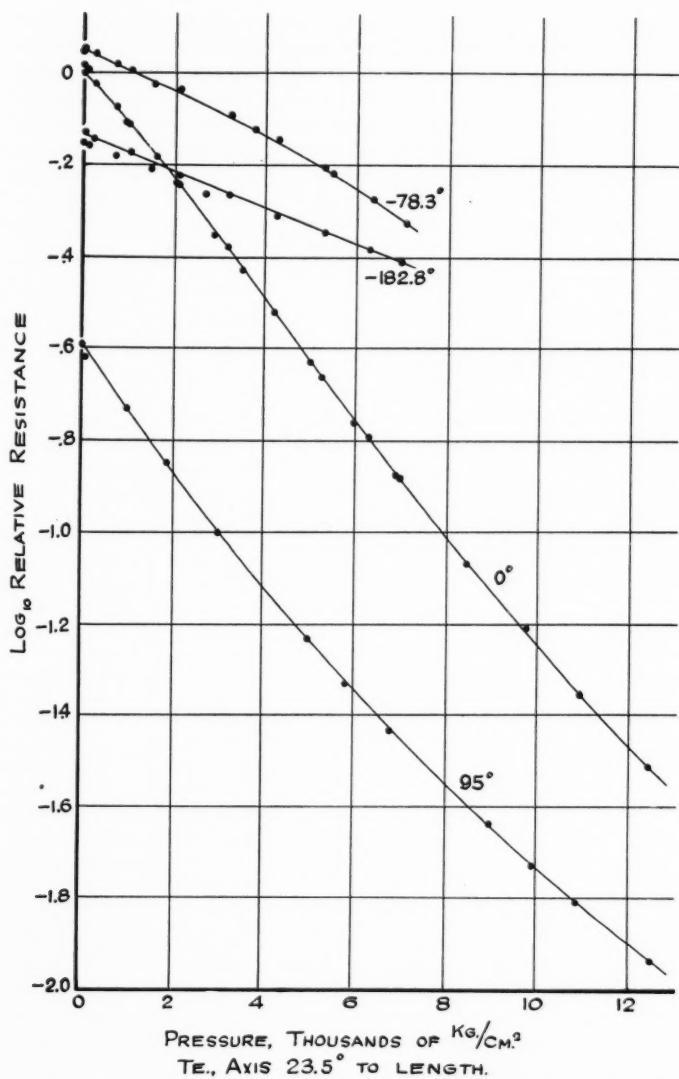
FIGURE 3.   Logarithm to the base 10 of the relative resistance of single crystal tellurium, axis 23.5° to the length, as a function of pressure at several temperatures.

sistance itself.   These are shown for the two orientations, axes at 86°
and 23.5° to the length, in Figures 2 and 3.   The ascending and de-
scending branches lay so closely together in general that no attempt
was made to separate them in the figures.   The low temperature run
of the 23.5° orientation does, however, show some divergence; the
points with decreasing pressure are the high lying points.   It is to
be noticed that the two independent runs at 0° lie on the same curve

TABLE VI.

TELLURIUM.

Pressure kg/cm²	$\log_{10}(R/R_0)$ (measured)				$\log_{10}(\rho/\rho_0)$ (specific)			
	$-182°.8$	$-78°.3$	$0°$	$95°$	$-182°.8$	$-78°.3$	$0°$	$95°$
86° between axis and length								
0	$-.213$	$-.032$	$.000$	$-.541$	$-.213$	$-.032$	$.000$	$-.541$
1000	$-.262$	$-.079$	$-.107$	$-.702$	$-.262$	$-.079$	$-.107$	$-.702$
2000	$-.310$	$-.127$	$-.229$	$-.853$	$-.310$	$-.127$	$-.229$	$-.853$
3000	$-.357$	$-.177$	$-.356$	$-.990$	$-.357$	$-.177$	$-.356$	$-.990$
4000	$-.406$	$-.230$	$-.490$	-1.122	$-.405$	$-.229$	$-.489$	-1.121
5000	$-.454$	$-.287$	$-.632$	-1.245	$-.453$	$-.286$	$-.631$	-1.244
6000	$-.503$	$-.351$	$-.772$	-1.363	$-.502$	$-.350$	$-.771$	-1.362
7000	$-.553$	$-.419$	$-.908$	-1.478	$-.552$	$-.418$	$-.907$	-1.477
8000			-1.038	-1.582			-1.037	-1.581
9000			-1.164	-1.681			-1.163	-1.680
10000			-1.290	-1.776			-1.289	-1.774
11000			-1.408	-1.865			-1.406	-1.863
12000			-1.520	-1.952			-1.518	-1.950
23°.5 between axis and length								
0	$-.135$	$+.047$	$.000$	$-.582$	$-.135$	$+.047$	$.000$	$-.582$
1000	$-.175$	$+.005$	$-.116$	$-.727$	$-.170$	$+.010$	$-.111$	$-\bullet.722$
2000	$-.215$	$-.038$	$-.239$	$-.863$	$-.205$	$-.028$	$-.229$	$-.853$
3000	$-.255$	$-.086$	$-.365$	$-.994$	$-.240$	$-.071$	$-.350$	$-.979$
4000	$-.295$	$-.137$	$-.498$	-1.119	$-.275$	$-.117$	$-.478$	-1.099
5000	$-.336$	$-.193$	$-.635$	-1.237	$-.311$	$-.168$	$-.610$	-1.212
6000	$-.376$	$-.257$	$-.768$	-1.347	$-.346$	$-.227$	$-.738$	-1.317
7000	$-.416$	$-.330$	$-.898$	-1.450	$-.382$	$-.296$	$-.864$	-1.416
8000			-1.022	-1.548			$-.983$	-1.509
9000			-1.134	-1.645			-1.090	-1.601
10000			-1.246	-1.735			-1.198	-1.687
11000			-1.357	-1.818			-1.304	-1.765
12000			-1.465	-1.896			-1.408	-1.839

indistinguishably. The numerical values of the logarithm of the relative resistance are given in Table VI in terms of the resistance at atmospheric pressure at $0°$ C of the two orientations. The table also contains the logarithms of the relative specific resistances, that is, the measured resistance corrected for the effect of pressure on dimensions. The relative specific resistances at atmospheric pressure have not, however, been corrected for the effect of thermal contraction. It will be noticed that the correction for distortion is almost negligible for the $86°$ orientation, but quite perceptible for the $23.5°$ orientation.

TABLE VII.

TELLURIUM.

Pressure kg/cm²	Log₁₀ ρ 0° between axis and length				Log₁₀ ρ 90° between axis and length			
	$-182°.8$	$-78°.3$	$0°$	$95°$	$-182°.8$	$-78°.3$	$0°$	$95°$
0	$-.564$	$-.389$	$-.450$	-1.046	$-.417$	$-.236$	$-.204$	$-.745$
1000	$-.592$	$-.413$	$-.561$	-1.178	$-.466$	$-.283$	$-.311$	$-.907$
2000	$-.625$	$-.449$	$-.678$	-1.303	$-.515$	$-.331$	$-.433$	-1.057
3000	$-.658$	$-.489$	$-.799$	-1.425	$-.562$	$-.381$	$-.560$	-1.194
4000	$-.690$	$-.533$	$-.923$	-1.541	$-.610$	$-.434$	$-.693$	-1.325
5000	$-.721$	$-.585$	-1.053	-1.652	$-.658$	$-.491$	$-.835$	-1.448
6000	$-.752$	$-.642$	-1.177	-1.752	$-.707$	$-.555$	$-.975$	-1.566
7000	$-.790$	$-.712$	-1.300	-1.848	$-.757$	$-.623$	-1.111	-1.681
8000			-1.416	-1.935			-1.241	-1.785
9000			-1.519	-2.027			-1.367	-1.884
10000			-1.622	-2.111			-1.493	-1.978
11000			-1.723	-2.186			-1.610	-2.067
12000			-1.827	-2.257			-1.722	-2.154

Table VII contains the logarithms of the actual specific resistances for the $0°$ and the $90°$ orientations, calculated by the same methods as for the other metals.

DISCUSSION.

This discussion will at first not be concerned with tellurium, which is only partially metallic in character, reserving this for later. Considering now only the true metals, the general effect of lowering temperature is the same as that found previously for the cubic metals.[1] In all cases, that is, for every orientation of every metal,

the pressure coefficient at liquid oxygen temperature is greater *numerically* than at CO_2 temperature; this holds both for the more normal metals and for arsenic, the resistance of which decreases with pressure, and also for bismuth and antimony with positive pressure coefficients. Excepting arsenic, the largest temperature effect is shown by the 90° orientation of antimony, the pressure coefficient of which at liquid O_2 temperature is more than double that at CO_2 temperature. These remarks apply to the linear term in the power series development in those cases in which such a development is possible. The second degree terms do not show any such regularity, but may either increase or decrease with decreasing temperature. Arsenic is anomalous because of the breaks in its pressure coefficient. Its coefficient in the upper pressure range at liquid O_2 temperature is of the order of three times greater than in any other range.

It is significant that in those cases in which departure from the second degree relation can be established the curvature becomes greater at increased pressure, provided the resistance decreases. On the other hand, bismuth and antimony, the resistance of which increases with pressure, have a decreasing curvature with increasing pressure. This result for the normal metals would suggest that the suspected minimum of resistance is nearer than would be indicated by an extrapolation of the second degree curves. The accuracy of the previous measurements for the cubic metals was not sufficient to indicate any such effect for them, and in fact most of the former results were linear.

A question which could not be put with regard to the cubic metals now presents itself, the question namely as to the relative effect of pressure on resistance in different directions. Is the effect of pressure to make the resistance in different directions more nearly alike, or does it accentuate the difference? The question can be answered at once by forming the derivative:

$$\frac{1}{F}\frac{dF}{dp} \equiv \frac{1}{\dfrac{\rho_{0°}}{\rho_{90°}}}\frac{d}{dp}\left(\frac{\rho_{0°}}{\rho_{90°}}\right) = \frac{1}{\rho_{0°}}\frac{d\rho_{0°}}{dp} - \frac{1}{\rho_{90°}}\frac{d\rho_{90°}}{dp}$$

We therefore have merely to take the difference of pressure coefficients in the two directions. When the ratio $\rho_{0°}/\rho_{90°}$ ($\equiv F$) is greater than unity, a negative value for the right hand side of the equation means that the resistance becomes more nearly equal under pressure. The results are given in Table VIII.

TABLE VIII.

EFFECT OF PRESSURE ON RATIO OF RESISTANCE IN DIFFERENT DIRECTIONS IN THE CRYSTAL.

Substance	Temp.	$\dfrac{1}{F}\dfrac{dF}{dp}$	$\dfrac{\rho_{0°}}{\rho_{90°}}$ at 0° C
Zn	− 78°.3	$-4.05\times10^{-6}p+14.4\times10^{-11}p^2$	1.038
	−182°.8	$-3.49\times10^{-6}p+11.5\times10^{-11}p^2$	
Cd	− 78°.3	$-3.35\times10^{-6}p+17.3\times10^{-11}p^2$	1.207
	−182°.8	$-2.04\times10^{-6}p+4.8\ \times10^{-11}p^2$	
Sn	− 78°.3	$-0.22\times10^{-6}p+\ 3.4\times10^{-11}p^2$	.695
	−182°.8	$-0.83\times10^{-6}p-\ 4.9\times10^{-11}p^2$	
		$\dfrac{\Delta F}{F}$	
Bi	− 78°.3	3000, +.0322; 7000, +.0970	1.267
	−182°.8	+.0530 +.0672	
Sb	− 78°.3	3000, +.0584; 7000, +.1570	
	−182°.8	+.0400 +.1071	.756

It is seen that pressure tends to equalize the resistance in different directions for Zn, Cd, and Sb, but for Bi and Sn it accentuates the differences. The effect of pressure in equalizing resistance becomes less marked at low temperatures for Zn, Cd, and Sb, whereas for Bi and Sn the effect of pressure in unequalizing resistance becomes greater at lower temperatures.

The behavior of antimony demands special consideration. The resistance of the 90° orientation at − 182.8° apparently passes through a very flat minimum at approximately 400 kg/cm², as may be found from a rough graphical construction of the data in the table. The initial pressure coefficient of resistance is therefore negative, and doubtless would become increasingly so at lower temperatures. This is to be contrasted with the maximum resistance at 50° previously found for the same orientation. It is obvious that if the high temperature curves previously found are to fit together with the low

temperature curves now found there must be a reversal of curvature
of the low temperature curves at sufficiently high pressure. It is
this which is evidently forshadowed by the decreasing curvature with
increasing pressure already commented on.

Finally, with regard to tellurium, the most striking feature is the
magnitude of the effect, the resistance at $95°$ at 12000 kg/cm² being
only about one per cent of the resistance at $0°$ at atmospheric pressure.
This is two or three times greater than the change which I found in
black phosphorus, the substance with the largest pressure effect which
I have yet measured. To a rough first approximation the logarithm
of resistance is linear in the pressure, that is, the rate of proportional
change with pressure is roughly the same at all pressures. Further-
more, the rate of change is approximately the same at $0°$ and $95°$, and
also the same at $-78.3°$ and $-182.8°$, the rate at the two latter
temperatures being very much less than at the two higher tempera-
tures. This difference of rate at the two lower temperatures demands
a crossing of the curves and a consequent reversal of sign of the tem-
perature coefficient as pressure rises. One might be inclined to suspect
a polymorphic transition between $0°$ and -78.3, but there is no
evidence for it, as shown by a special run in which resistance was
measured as a function of temperature at atmospheric pressure, and
also by the fact that there were no irreversible changes on running
the temperature back and forth. The special temperature run showed
for the $23°.5$ orientation a smooth maximum of resistance at about
$-45°$ C.

To a second approximation, the logarithm of the resistance is not
linear in pressure. At $0°$ there is reversal of curvature; at low pres-
sures the curve is concave downward, but at high pressures it is
concave upward, while the $95°$ curve is concave upward at all pressures.
Curvature in this direction is necessary if pressure is to pass through
a minimum with rising pressure, but any such minimum must be very
remote as far as any present indications are concerned, the immediate
effect of pressure at these temperatures being a continuous decrease
of resistance towards that characteristic of true metals. The curve
at $-78.3°$ is in some respects not unlike that at $0°$; it starts out con-
cave downward, and apparently will cross the $-182.8°$ curve at
pressures not very far beyond those reached, with consequent addi-
tional complications in the behavior of the temperature coefficient.

The effect of pressure on the resistance of tellurium is not greatly
different in the different directions, as may be seen by comparison of
figures 2 and 3. There is some difference in the order of the curves

for different temperatures at low pressures, indicating that the reversal of sign of the temperature coefficient of resistance occurs at different temperatures in different directions, and there are also differences in the numerical values, but on the whole the resemblances in the different directions are more striking than are the differences. This leads to the conclusion that the very large effect of pressure on the resistance is not intimately connected with the crystal structure.

Examination of Table VII shows that the difference between different directions in the crystal becomes less marked as pressure increases at all temperatures.

I am much indebted to Mr. Charles Chase for setting up the apparatus and regulating the temperature controls for the low temperature measurements, and to Mr. L. H. Abbot for making the measurements of the resistance of tellurium at the higher pressures. I am also indebted to the Milton Fund of Harvard University for financial assistance.

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